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Gas Chromatographic Method for Quantitative Determination of C2 to C13 Hydrocarbons in Roadway Vehicle Emissions

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16. ABSTRACT

A gas chromatographic system was used to quantitate more than 300 gas-phase hydrocarbons from background and roadside ambient air samples. Samples were simultaneously collected in Tedlar bags and on Tenax cartridges. Hydrocarbons from Tedlar bag-collected samples were quantitated on a gas chromatograph arranged in a dual column configuration and equipped with a flame ionization detector. The C_2 and C_3 hydrocarbons were separated on a 5-m long stainless steel column packed with silica gel; C_4 to C_{13} hydrocarbons were separated on a 125-m long glass capillary column containing 7.5% hydrophobic silica. A stainless steel hydrocarbon trap filled with untreated glass wool permitted the concentration of at least 4-L of sample at 70% relative humidity. This extends the detection limits for individual hydrocarbons to 15.0 parts per trillion carbon. A programmable valve controller maintained trap cooling during hydrocarbon concentration and thermally desorbed the hydrocarbons for gas chromatographic analysis.

Hydrocarbons collected on Tenax cartridges were analyzed by gas chromatography/mass spectrometry. More than 200 hydrocarbons in roadside air samples were partially or completely identified.

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Gas Chromatographic Method for Quantitative Determination of C_2 to C_{13} Hydrocarbons in Roadway Vehicle Emissions

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A gas chromatographic system was used to quantitate more than 300 gas-phase compounds, as hydrocarbons, from roadside ambient air samples. Samples were simultaneously collected in Tedlar bags and on Tenax cartridges. Hydrocarbons from Tedlar bag collected samples were quantitated on a gas chromatograph arranged in a dual column configuration and equipped with a flame ionization detector. The C_2 and C_3 hydrocarbons were separated on a 5 m long stainless steel column packed with silica gel. C_4 to C_{13} hydrocarbons were separated on a 125-m long glass capillary column containing 7.5% hydrophobic silica. A stainless steel subambient hydrocarbon trap filled with untreated glass wool permitted the concentration of at least 4 L of sample at 70% relative humidity. A temperature controller cooled the trap for hydrocarbon concentration and thermally desorbed the hydrocarbons for gas chromatographic analysis. This trap extends the detection limits for most hydrocarbons to 15.0 parts per trillion (pptr) carbon. Hydrocarbons collected on Tenax cartridges were analyzed by gas chromatography/mass spectrometry in order to provide qualitative identification for the peaks obtained from the GC analysis. More than 90% of the compounds in roadside air samples were partially or completely identified.

Several studies have been conducted on the emission of organic gases from diesel- and gasoline-fueled engines (*1–4*). Gas-phase hydrocarbons emitted from diesel- and gasoline-fueled engines have been studied by using various solid trapping media (*5–10*) and hydrocarbon desorption techniques (*5, 10, 11*), cold traps (*12–14*), and bag collection (*8, 15–20*). Gas-phase hydrocarbon concentration using solid media and cold trapping techniques have certain limitations. Commonly used solid absorbents such as the Tenax and Chromosorb series of polymers are not quantitative below C_8 carbon number (*11, 21*). Cold traps are manpower intensive and not readily adaptable for collecting multiple roadside samples. Both absorbents are also subject to artifact formation (*11*).

Gaseous hydrocarbon emissions from motor vehicles are of concern primarily because these hydrocarbons participate as oxidant precursors in atmospheric photochemical systems (*17, 19, 22–24*). These transportation-related pollutants have been characterized as one of the most significant air pollution problems. Quantitative speciation of vehicle hydrocarbon emissions is also of interest because of their potential toxicity and carcinogenicity (*7, 24, 25*). Benzene, a compound present in both raw gasoline and vehicle emissions, is listed as a hazardous pollutant under Section 112 of the Clean Air Act.

Several reports on gaseous hydrocarbon emission studies (*8, 26–30*) list chromatographic identification (largely retention times) of up to 100 compounds. At least two studies have used gas chromatographic/mass spectrometry (GC/MS) techniques to identify at least 100 compounds. A GC/MS study in the Allegheny Mountain Tunnel of the Pennsylvania Turnpike (*31*) detected 400 vehicle-related compounds and partially or completely identified more than 300 gas-phase hydrocarbons larger than C_4.

In this study, a dual column (packed and capillary) GC system was used for the quantitation of more than 300 vehicle emission products in the C_2 to C_{13} hydrocarbon range. This GC method is sufficiently sensitive to routinely detect individual hydrocarbons at the 15.0 pptr carbon (C) level and quantitate individual hydrocarbons at the 22.0 pptr C level.

EXPERIMENTAL SECTION

Sampling. Gas samples were collected in Tedlar bags (E. I. du Pont de Nemours and Co., Wilmington, DE) (*18, 32, 33*). New bags were flushed four to five times with zero air to eliminate contamination problems (*15, 17, 26*).

Trapping System. Hydrocarbons in the gas samples were concentrated in identical 15.2 cm × 2.2 mm inside diameter (i.d.) traps (Figure 1) firmly packed with 10.2 cm of glass wool rather than with the small-diameter glass beads typically used as adsorbent (*17, 18*). Roadside humidity levels limited the concentration (glass bead adsorbent) of gaseous volumes to less than 500 mL. Exploratory evaluations of background and roadside samples using glass beads indicated that a minimum background sample collection volume of 1500 mL was necessary to provide adequate concentrations for individual hydrocarbon background corrections to the roadside samples.

A Nutech Model 320 controller (Nutech, Inc., Durham, NC) maintained concentration and desorption temperatures in both individually controlled traps and heated the 0.8 mm i.d. stainless steel tubing that connected the traps to the switching valves. The traps and all heated lines were wrapped with insulation tape. The Nutech controller was set to −170 °C (temperature maintained by using liquid nitrogen) for C_2 and C_3 concentrations and to −135 °C for C_4 to C_{13} concentration. Two minutes was required to bring the trap temperature from −170 °C to 150 °C.

Both traps were back flushed with helium at 500–600 mL/min at a trap temperature of 150 °C for at least 45 min. All sample transfer lines were heated to 120 °C to minimize hydrocarbon condensation in the GC inlet system.

GC System. The GC system (Figure 2) utilized a flame ionization detector (FID) and an automatic data processing terminal (Model 5880A, Hewlett-Packard) operated in a dual column configuration. One column was a 5 m × 2.2 mm i.d. section of stainless steel packed with 60–80 mesh, grade 59 silica gel (Davison Chemical, Baltimore, MD). This column, for C_2 and C_3 component analysis, was operated at 30 °C and at a helium flow rate of 30 mL/min. The C_4 to C_{13} hydrocarbons were separated on a 125 m × 0.5 mm i.d. soft glass 7.5% hydrophobic silica capillary column (Quadrex, Corp., Amity Station, New Haven, CT). The hydrogen carrier gas flow was maintained at 7.00 mL/min by a Tylan RO-14-100 mass flow controller (Tylan, Corp., Torrence, CA). Column temperature was maintained (by using liquid nitrogen) at −80 °C until the hydrocarbons were flushed from the trap. The oven temperature was then programmed to increase to −10 °C at a rate of 20.0 °C/min (no hold time at −10 °C) followed by an increase to 120 °C at a rate of 3.5 °C/min (15-min hold at 120 °C).

GC Control and Data Terminal. The GC was equipped with a keyboard terminal used to control oven temperature programming and data acquisition, integration parameters, and the air- and vacuum-actuated Seiscor valves. A combination of manual

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Table I. Analytical Repeatability

injection	hydrocarbon, ppb C					
	ethane	ethylene	propane	acetylene	propylene	gasoline
1	*a*	*a*	205.9	131.9	178.9	658.9
2	127.5	69.4	200.7	131.1	178.7	679.7
3	116.2	59.2	197.2	129.4	175.0	643.2
4	138.1	77.4	199.8	129.7	178.0	654.9
5	126.9	69.7	188.3	125.4	171.1	659.1
6	115.8	61.7	190.0	126.0	168.9	654.9
av, $\bar{X}$	124.9	67.5	197.0	128.9	175.1	658.4
RSD[b]	9.3	7.2	6.7	2.7	4.2	11.9

[a] Cylinder contaminant interference. [b] Relative standard deviation.

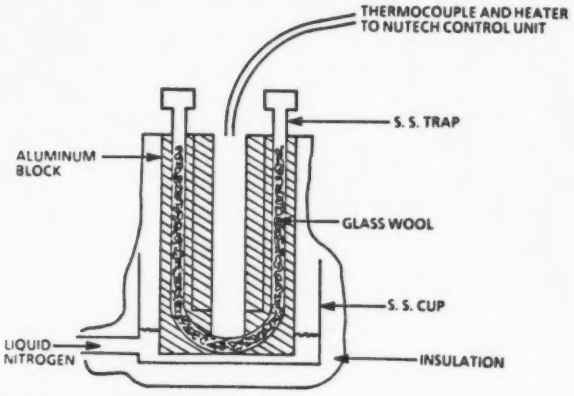

Figure 1. Hydrocarbon trap.

and Seiscor valves were used for sampling and analysis. The Seiscor Model VIII six-port switching valves (Seiscor Division, Seismograph Service, Corp., Tulsa, OK) were mounted in an oven on top of and insulated from the GC oven. These valves were maintained at 90 °C.

Standard Preparation. Experiments were performed with gasoline and pure individual liquid and gaseous hydrocarbons. A vaporization system was setup with a metered air flow (zero grade) for the injection of liquid gasoline and pure hydrocarbon samples. The vaporizer consists of a 61 cm × 5.3 mm i.d. length of insulated stainless steel tubing with a purging GC liquid injection port through which liquid samples (gasoline and individual hydrocarbons) were introduced to prepare known hydrocarbon levels. The injector was located 40 cm from the exit end of the system. The vaporizer was heated to 240 °C, and a Teledyne Hasting-Raydist Model NALL 5K mass flowmeter was used to monitor mixing air flow.

Pure gaseous ethane, ethylene, propane, acetylene, and propylene were used to determine the repeatability of sample preparation and analysis, trap collection efficiency, and response factors for the C_2 and C_3 system. Dilute concentrations of vaporized gasoline were used for the repeatability study for C_4 to C_{13} hydrocarbons; the levels were prepared to approximate roadside hydrocarbon concentrations.

Standards were prepared by injecting a known liquid hydrocarbon volume into the heated vaporizer air stream (total bag air volume calculated). A gaseous aliquot of the concentrated sample was then transferred (with a gastight syringe) to a second Tedlar bag containing a known volume of zero air for dilution to desired concentrations. Dilute concentrations were achieved by changing liquid or pure gas injection, concentrate bag, and dilute bag volumes.

Analytical Integrity. The stability of C_4 to C_{13} hydrocarbons in Tedlar bags over a 6-h period was evaluated by repeatedly analyzing a 1155.6-mL aliquot of an ambient air sample collected at 1 L/min for 1 h in a Tedlar bag.

The extent of residual hydrocarbon buildup in the C_4 to C_{13} system was evaluated by alternately analyzing 1414.5-mL samples of 796.6 ppb C dilute vaporized gasoline and zero air. Benzene

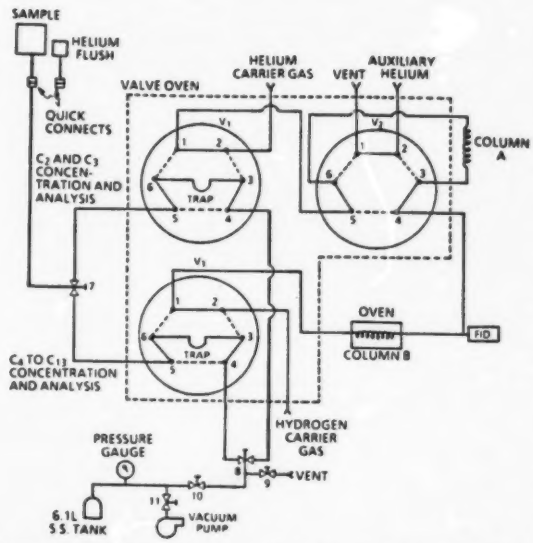

Figure 2. GC system: V_1, V_2, and V_3, Seiscor switching valves in the off position; 7, 8, three-way needle valves; 9, 10, and 11, two-way needle valves; column A, silica gel-packed column; column B, capillary column.

and toluene (1.5% and 14.0% of the total gasoline concentration, respectively) were chosen for evaluation because they were relatively free from other hydrocarbon interferences. The C_2 and C_3 system was also tested by alternately analyzing a laboratory-prepared hydrocarbon mixture and zero air. These tests, in conjunction with the repeatability studies, confirm analytical integrity by the absence of HC absorption and complete desorption by the system.

Detection and Quantitation Limits. Chromatograpic limits of detection and quantitation for C_2 and C_3 and C_4 to C_{13} (*34*), were established by using the hydrocarbon contaminants present in the zero air. The zero air supply was first surveyed and the contaminants were identified. Analysis for hydrocarbons and concentrations indicated ethylene to be the C_2 and C_3 and *n*-heptane to be the C_4 to C_{13} representative hydrocarbon choices. The sample bag was cleaned (evacuated and air purged) and refilled from the air cylinder for each analysis to prevent external influences.

Hydrocarbon Response. The C_2 and C_3 hydrocarbon response data were derived by preparing known quantities of acetylene (no background in present zero air supply) at levels from 0.17 to 54.80 ppb C. The analyses were conducted over a 4-week period, and a total of 39 values were obtained.

Quantitative capillary system (C_4 to C_{13}) hydrocarbon response was established using several individual standards (PolyScience Corp., Niles, IL): *n*-pentane, 2,2-dimethylbutane, methylcyclohexane, isooctane, and *n*-nonane. These hydrocarbons were selected as they were present in roadside samples, readily available, and not present in the existing supply of zero air used to prepare the dilute concentrations. The study was conducted over a 4-week

Table II. Hydrocarbon Stability in Tedlar Bags

	hydrocarbon, ppb C								
run time	*n*-butane	benzene	heptane	isooctane	toluene	ethylbenzene	C_9H_{12}	naphthalene	total sample
0922	127.93	43.46	17.21	35.35	152.48	17.72	32.23	4.33	1644.56
1048	118.20	43.26	17.18	34.61	151.31	18.17	32.18	3.39	1626.19
1218	111.69	43.18	17.51	34.91	150.47	18.90	31.76	3.56	1719.94
1348	128.61	43.33	17.59	35.09	150.75	18.98	31.67	3.77	1740.19
1516	*a*	43.09	17.19	34.71	151.03	18.09	31.58	2.59	1678.12
av, $\bar{X}$	121.61	43.28	17.34	34.91	151.20	18.38	31.88	3.52	1681.88
RSD[b]	8.14	0.15	0.19	0.26	0.77	0.54	0.30	0.64	4.84

[a] Cylinder contaminant interference. [b] Relative standard deviation.

Table III. Instrument Limits of Detection and Quantitation

analysis	ethylene, ppb C	*n*-heptane, ppb C
1	0.296	0.011
2	0.290	0.014
3	0.304	0.011
4	0.322	0.011
5	0.305	0.013
6	0.276	0.011
7	0.306	0.012
av, $\bar{X}$	0.300	0.012
std dev, *s*	0.014	0.001
LOD[a]	0.342	0.015
LOQ[b]	0.440	0.022

[a] LOD, limit of detection. Average + 3 standard deviation units. [b] LOQ, limit of quantitation. Average + 10 standard deviation units.

period (total of 127 values), with prepared concentration levels ranging from 0.04 to 56.16 ppb C.

System Linearity. Acetylene was used for the C_2 and C_3 linearity study, with prepared concentrations predominantly less than 30 ppb C. Previous roadside samples had shown this to be the level for more than 85% of the individual hydrocarbons when the total sample was in the 500- to 700-ppb C range. Analytical linearity for the capillary system was similarly established with known concentrations of *n*-pentane, 2,2-dimethylbutane, methylcyclohexane, isooctane, *n*-nonane, *n*-butylbenzene, *n*-undecane, and *n*-hexylbenzene.

Tedlar Bag Sampling. Collecting hydrocarbon samples in fluorocarbon bags often results in contamination problems (*15, 17, 18, 32*). Preliminary GC evaluations of individual hydrocarbon standards collected in Tedlar bags showed that the samples were contaminated. A major contaminant was identified by GC/MS as *N,N*-dimethylacetimide (DMAC). Experiments showed that by increasing the trap's helium backflush to 500–600 mL/min for 45 min, the analytical interference of DMAC was reduced to an insignificant level at maximum instrument sensitivity. This indicated that the problem resulted from DMAC adsorption on the trap during multiple sampling periods. This was further evidenced by the absence of the DMAC peak after a long flushing period.

Gas Chromatography/Mass Spectrometry. Ambient air samples, along the roadside, were also collected in Tenax cartridges and analyzed by GC/MS with thermal desorption in order to provide for the qualitative identification of the peaks obtained from the GC. These Tenax samples were collected concurrently with the bag samples.

Tenax cartridges were prepared by packing a nickel 200 tube (100 mm × 12 mm i.d.) with 1.35 g of 60/80 mesh Tenax held in place by heat-treated silanized glass wool. Prior to sampling, each packed cartridge was thermally desorbed in a nitrogen stream at 270 °C for 4 h. The cartridges were then allowed to cool to ambient temperature while still being purged with nitrogen and then two cartridges were sealed in aluminum sampling cartridge holders in a nitrogen atmosphere until required for sampling.

The GC/MS with thermal desorption consisted of a Nutech Model 320 Tenax cartridge desorption unit interfaced to a Hewlett-Packard Model 5992A GC/MS system by a heated stainless steel transfer line (150 mm × 0.8 mm i.d.) coated with OV-17. The transfer line was connected directly to the front of the 125 m Quadrex column in the GC oven.

The thermal desorption from the Tenax was performed by back flushing the cartridge at 240 °C with a 15 mL/min helium flow into a liquid nitrogen cooled trap in the Nutech unit. After 7 min the cold trap was rapidly heated to 190 °C (3 min) and at the same time a six-port valve was switched to allow the helium carrier gas to direct the vaporized material to the front of the GC column.

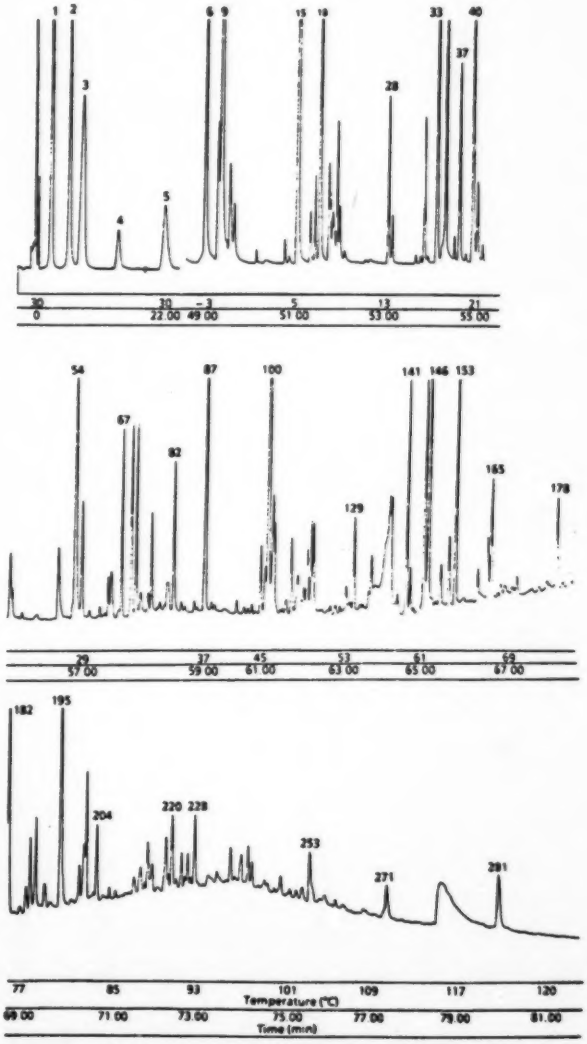

Figure 3. Typical chromatogram for dilute gasoline sample. Peak numbers correspond to those listed in Table IV.

Table IV. GC/MS Identification of Roadside Sample Hydrocarbons

no.	compound
*1[a]	ethane
*2	ethylene
*3	propane
*4	acetylene
*5	propylene
*6	isobutane
*7	1-butene
*8	2-methylpropene
*9	*n*-butane
*10	1,3-butadiene
*11	*trans*-2-butene
*12	*cis*-2-butene
13	N[b]
*14	3-methyl-1-butene
*15	2-methylbutane (isopentane)
*16	1-pentene
*17	2-methyl-1-butene
*18	*n*-pentane
*19	*trans*-2-pentene
*20	*cis*-2-pentene
21	2-methyl-1,3-butadiene
*22	2-methyl-2-butene
*23	cyclopentane
24	1-*trans*-3-pentadiene
25	1-*cis*-3-pentadiene
26	3,3-dimethyl-1-butene
27	N
*28	2,2-dimethylbutane
29	3-methyl-1-pentene
*30	4-methyl-1-pentene
31	2,3-dimethylbutane
32	4-methyl-*cis*-2-pentene or 2,3-dimethyl-1-butene
33	2-methylpentane
34	C_6H_{10} isomer
35	3-methylpentane
36	2-methyl-1-pentene
*37	methylcyclopentane
38	1-hexene
39	2-ethyl-1-butene
*40	*n*-hexane
41	3-methyl-*cis*-2-pentene
42	*cis*-3-hexene
43	*cis*-2-hexene
44	3- or 4-methylcyclopentene
45	cyclohexane
46	3-methyl-*trans*-2-pentene
47	C_6H_8 isomer
48	cyclohexene
49	C_6H_{10} isomer
50	C_6H_{10} isomer
51	1,4-hexadiene
52	1-methylcyclopentene
53	N
*54	benzene
55	2,2-dimethylpentane
56	2,2,3-trimethylbutane
57	2,4-dimethylpentane
58	1,1-dimethylcyclopentane
59	2,4-dimethyl-1-pentene
60	3,3-dimethylpentane
61	3,4-dimethyl-1-pentene
62	3,4-dimethyl-*cis*-2-pentene
63	5-methyl-2-hexene
64	1-*cis*-3-dimethylcyclopentane
65	1-*trans*-3-dimethylcyclopentane
66	3-ethyl-1-pentene
67	2,3-dimethylpentane
68	C_7H_{14} isomer
69	U[c]
70	2-methylhexane
71	3-methylhexane
72	3-ethylpentane
73	1-*cis*-2-dimethylcyclopentane
74	methylcyclohexane
75	3-methyl-*cis*-2-hexene
76	1-heptene
77	3-ethyl-2-pentene
78	C_7H_{12} isomer
79	ethylcyclopentane
80	C_7H_{14} isomer
81	C_7H_{14} isomer
82	*n*-heptane
83	*trans*-2-heptene
84	*trans*-3-heptene
85	C_7H_{12} isomer
86	U
*87	2,2,4-trimethylpentane (isooctane)
88	1,1,3-trimethylcyclopentane
89	C_8H_{16} isomer
90	C_7H_{12} isomer
91	2,2,4-trimethyl-1-pentene
92	trimethylcyclopentane
93	N
94	C_7H_{12} isomer
95	trimethylcyclopentane
96	2,2-dimethylhexane
97	2,2,3-trimethylpentane
98	2,4-dimethylhexane
99	2,5-dimethylhexane + C_8H_{16} isomer
*100	toluene
101	2,3,4-trimethylpentane
102	trimethylcyclopentane
103	dimethylcyclohexane
104	trimethylpentane
105	C_8H_{18} isomer
106	2,3-dimethylhexane
107	U
108	methylethylcyclopentane
109	U
110	U
*111	4-methylheptane
112	2-methylheptane
113	3-methylheptane
114	C_8H_{14} isomer + unknown compound(s)
115	3-ethyl-1,4-hexadiene + unknown compound(s)
116	isopropylcyclopentane
117	methylethylcyclopentane
118	dimethylcyclohexane
119	dimethylhexane
120	octene
121	C_8H_{16} isomer
122	methylethylpentane
123	C_8H_{16} isomer
124	1-octene
125	*trans*-4-octene
126	n-octane
127	C_8H_{16} + C_8H_{14} isomers
128	C_8H_{16} + C_8H_{14} isomers
129	2,2,5-trimethylhexane
130	N
131	octyne
132	2,2,4-trimethylhexane
133	2,2,4- or 3,3,4-trimethylhexane
134	N
135	dimethylheptene
136	2,3,5-trimethylhexane
137	C_9H_{16} isomer
138	C_9H_{18} isomer
139	4-ethyl-3-heptene
140	2,3,3-trimethylhexane
*141	ethylbenzene
142	dimethylheptane
143	2-methyl-4-ethylhexane
144	2,5- or 3,5-dimethylheptane
*145	*p*-xylene
146	*m*-xylene
147	2-methyl-3-ethylhexane
148	4-ethylheptane
149	C_9H_{16} isomer
150	2-methyloctane
151	methylethylcyclohexane
152	2-methyloctane
*153	*o*-xylene
154	4-methyloctane
155	C_9H_{18} isomer
156	C_9H_{16} + C_9H_{18} isomers
157	C_9H_{16} + C_9H_{18} isomers
158	C_9H_{18} isomer
159	C_9H_{18} isomer
160	trimethylcyclohexane
161	C_9H_{18} isomer
162	C_9H_{18} isomer
163	iso- or *n*-propylcyclohexane
164	C_9H_{18} isomer
*165	*n*-nonane
166	U
167	N
168	N
169	2,2,4-trimethylheptane
170	3,3,5-trimethylheptane
171	isopropylbenzene
172	5-methylnonane
173	$C_{10}H_{22}$ isomer
174	$C_{10}H_{22}$ isomer
175	$C_{10}H_{22}$ isomer
176	$C_{10}H_{22}$ isomer
177	$C_{10}H_{22}$ isomer
178	*n*-propylbenzene
179	$C_{10}H_{22}$ isomer
180	2,3-dimethyloctane
181	$C_{10}H_{22}$ isomer
182	1-methyl-3- or 4-ethylbenzene
183	$C_{10}H_{22}$ isomer
184	$C_{10}H_{22}$ isomer
185	$C_{10}H_{22}$ isomer
186	$C_{10}H_{22}$ isomer
187	$C_{10}H_{22}$ isomer
188	1-methyl-2-ethylbenzene
189	1,3,5-trimethylbenzene
190	$C_{10}H_{22}$ isomer
191	$C_{10}H_{22}$ isomer
192	$C_{10}H_{22}$ isomer
193	$C_{10}H_{22}$ isomer
194	$C_{10}H_{22}$ isomer
195	1,2,4-trimethylbenzene
196	$C_{10}H_{22}$ isomer
197	$C_{10}H_{22}$ isomer
198	$C_{10}H_{22}$ isomer
199	$C_{10}H_{22}$ isomer
200	$C_{10}H_{22}$ isomer
*201	*n*-decane
202	*sec*-butylbenzene
203	methylstyrene or indan
204	1,2,3-trimethylbenzene
205	$C_{11}H_{24}$ isomer
206	$C_{11}H_{24}$ isomer
207	1-methyl-3-isopropylbenzene
208	1-methyl-3-isopropylbenzene
209	$C_{11}H_{24}$ isomer
210	$C_{11}H_{24}$ isomer
211	N
212	C_4 alkylbenzene
213	U
214	C_4 alkylbenzene
215	C_4 alkylbenzene
216	C_4 alkylbenzene
217	$C_{11}H_{24}$ isomer
218	$C_{11}H_{24}$ isomer
219	$C_{11}H_{24}$ isomer
220	C_4 alkylbenzene
221	$C_{11}H_{24}$ isomer
222	$C_{11}H_{24}$ isomer
223	$C_{11}H_{24}$ isomer

Table IV (Continued)

no.	compound	no.	compound	no.	compound
224	C_4 alkylbenzene	249	C_5 alkylbenzene	277	U
225	C_4 alkylbenzene	250	C_2 alkylstyrene or methylindan	278	C_2 alkylstyrene or C_2 alkylindan
226	$C_{11}H_{24}$ isomer	251	C_5 alkylbenzene	279	C_4 alkylstyrene or C_3 alkylindan
227	C_4 alkylbenzene	252	C_5 alkylbenzene	280	U
228	C_4 alkylbenzene	253	2-phenyl-3-methylbutane	281	C_{12} paraffin
229	$C_{11}H_{24}$ isomer	254	C_5 alkylbenzene	282	C_3 alkylstyrene or C_2 alkylindan
230	N	255	methylindene	283	C_5 alkylbenzene
*231	*n*-undecane	256	C_5 alkylbenzene	284	C_3 alkylstyrene or C_2 alkylindan
232	C_5 alkylbenzene	257	C_5 alkylbenzene	285	$C_{13}H_{28}$ isomer
233	1,2,4,5-tetramethylbenzene	258	C_3 alkylstyrene or C_2 alkylindan	286	$C_{13}H_{28}$ isomer
234	$C_{11}H_{24}$ isomer	259	C_3 alkylstyrene or C_2 alkylindan	287	C_3 alkylstyrene or C_2 alkylindan
235	1,2,3,5-tetramethylbenzene	260	C_5 alkylbenzene	288	C_6 alkylbenzene
236	U	261	U	289	C_6 alkylbenzene
237	$C_{11}H_{24}$ isomer	262	C_3 alkylstyrene or C_2 alkylindan	290	C_6 alkylbenzene
238	C_2 alkylstyrene or methylindan + C_4 alkylbenzene	263	C_3 alkylstyrene or C_2 alkylindan + paraffin	291	C_6 alkylbenzene
		264	N	292	C_6 alkylbenzene
239	C_2 alkylstyrene or methylindan + C_4 alkylbenzene	265	2-phenyl-2-methylbutane	293	C_6 alkylbenzene
		266	C_5 alkylbenzene	294	C_6 alkylbenzene
240	C_5 alkylbenzene	267	C_5 alkylbenzene	295	U
241	1,2,3,4-tetramethylbenzene	268	C_5 alkylbenzene	296	*n*-tridecane
242	C_2 alkylstyrene or methylindan	269	C_3 alkylstyrene or C_2 alkylindan	297	$C_{14}H_{30}$ isomer
243	U	*270	*n*-dodecane + C_5 alkylbenzene	298	U
244	C_5 alkylbenzene + unknown compound(s)	*271	naphthalene	299	methylnaphthalene
		272	C_5 alkylbenzene	300	C_5 alkylbenzene
245	C_5 alkylbenzene + unknown compound(s)	273	benzothiophene	301	methylnaphthalene
		274	U	302	C_5 alkylbenzene
246	C_2 alkylstyrene or methylindan	275	U	303	C_5 alkylbenzene
247	C_2 alkylstyrene or methylindan	276	C_5 alkylbenzene	304	C_5 alkylbenzene
248	U			305	C_5 alkylbenzene

*Asterisk indicates verified by standard. [b]N, not detected by GC/MS. [c]U, unresolved peak by GC/MS.

The chromatographic column was held at −20 °C for 5 min and then the oven temperature was then programmed at a rate of 5 °C/min to 170 °C. The carrier gas flow rate was 4.00 mL/min as controlled by a Matheson Model 8240 mass flow controller. The total ion chromatogram obtained was comparable to the chromatogram obtained from the GC analysis. Identifications were made by comparing GC/MS results with published data bases (*35*, *36*) and with retention times and mass spectral data of standard compounds.

RESULTS AND DISCUSSION

The C_2 and C_3 repeatability data (Table I) were obtained from standards prepared by a single operator using individual gases. The ethane, ethylene, and propane variability resulted from the presence of unidentified contaminants in the zero air used to make the dilutions. No zero air contaminants were present in the acetylene or propylene elution zones. The latter values would therefore be a more reliable reflection of the repeatability.

The C_4 to C_{13} multicomponent (vaporized gasoline sample) repeatability is also shown in Table I. The parts per billion carbon values represent the sum of the individual hydrocarbon quantitation. Since the sample preparations were made over a several-week period (by two operators), the analytical precision indicates satisfactory preparation techniques and instrument stability.

The stability of several representative hydrocarbons in Tedlar bags is shown in Table II. These results correspond to observations of other researchers (*15*). In Table II, the compounds *n*-butane and naphthalene showed the greatest variability, this variability was related to the degree of interference by hydrocarbons with similar retention time. Total sample variability over this 6-h period was considered satisfactory.

Neither benzene nor toluene showed a response level increase in the analyzed zero air sample from the initial air sample to the final sample in the C_4 to C_{13} hydrocarbon buildup study. Results indicated satisfactory sampling and analytical integrity. The C_2 and C_3 system also showed the same analytical integrity. The analytical repeatability studies futher confirm the absence of hydrocarbon buildup in the system.

Table III, blank air cylinder values, shows the limits of detection (average + three standard deviation units) and quantitation (average + 10 standard deviation units) for the dual column system. The C_4 to C_{13} limits of detection were substantially less than the C_2 and C_3 limits (detection 0.015 vs. 0.342 ppb C and quantitation 0.022 vs. 0.440 ppb C). This would be expected when the analytical efficiency of a packed column is compared with a capillary column system.

The C_2 and C_3 hydrocarbon response data had a mean of 0.40 ppb C per count (normalized to 474 mL) and a standard deviation of ±0.04 ppb C per count. The C_4 to C_{13} hydrocarbon response data mean was 0.42 ppb C per count with a standard deviation of ±0.03 ppb C per counts (also normalized to 474 mL). This reproducibility was considered very satisfactory considering the number of hydrocarbon standards prepared and concentration range over which the data were obtained.

A linear regression plot for acetylene (correlation coefficient of 0.99) indicates a linear system response from 0.17 to 54.80 ppb C. The injected values were calculated based on hydrocarbon density and preparation volumes. Response values were calculated by using the previously determined hydrocarbon response factor.

Regression plots for *n*-pentane, 2,2-dimethylbutane, methylcyclohexane, isooctane, *n*-nonane, *n*-butylbenzene, *n*-undecane, and *n*-hexylbenzene indicate no linearity problems for the C_5 to C_8 compounds from 0.04 to 60 ppb C. Plots for both *n*-nonane (C_9) and *n*-butylbenzene (C_{10}) showed a slight decrease in response after 25 ppb C. Plots also showed *n*-undecane (C_{11}) to be linear through 10 ppb C and *n*-hexylbenzene (C_{12}) linear through 6 ppb C.

Operating parameters were adjusted to concentrate roadside samples to achieve a total non-methane level in the 500–700 ppb C range to prevent hydrocarbon extention into a nonlinear response situation. Sample size was based on carbon monoxide

(CO) analysis, as a relationship between total non-methane hydrocarbon had been established with this emission product previously.

Figure 3 is a chromatogram for a dilute vaporized gasoline sample. Most of the major hydrocarbons are labeled using the Table IV GC/MS identification scheme.

The quality assurance experiments for repeatability, stability, detection and quantitation limits, and linearity indicate the analytical system to be useful for the routine quantitation of hydrocarbons in the C_2 to C_{13} range.

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